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(51) International Patent Classification ⁷ : C08F 4/80, 4/06, 263/04, C08K 3/14, 3/22		A1	(11) International Publication Number: WO 00/46257 (43) International Publication Date: 10 August 2000 (10.08.00)
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(54) Title: METATHESIS-ACTIVE ADHESION AGENTS AND METHODS FOR ENHANCING POLYMER ADHESION TO SURFACES			
(57) Abstract The invention discloses an adhesion agent composition comprising at least one C ₃ -C ₂₀₀ olefin compound having at least one metathesis active double bond, wherein the olefin is substituted or unsubstituted; and at least one compatibilizing functionality for interacting with a substrate surface. The substrate surface can be any surface, for example, silicate glasses, silicate minerals, metals, metal alloys, ceramics, natural stones, plastics, carbon, silicon, and semiconductors. The invention also discloses articles of manufacture utilizing these adhesion agents as well as methods for adhering a polyolefin to a substrate surface.			

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METATHESIS-ACTIVE ADHESION AGENTS AND METHODS FOR ENHANCING POLYMER ADHESION TO SURFACES

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FIELD OF THE INVENTION

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The invention is directed generally to novel adhesion agents that enhance the adhesion of polymers to various substrate surfaces. More specifically, the invention relates to novel adhesion agents that comprise olefin compounds having a metathesis-active double-bond and to methods for enhancing the surface adhesive properties of ring opening metathesis polymerized (ROMP) polymers using such adhesion agents.

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BACKGROUND OF THE INVENTION

It is advantageous in many commercial applications to have strong adhesion between polymers (e.g., plastic resin coatings) and various substrate surfaces. Polymer coatings may be used, for example, to protect underlying surfaces from environmental and atmospheric conditions. In this manner, polymer coatings are useful in increasing the durability and extending the "life" of various surfaces, including glass optical fibers and mirrors. Adhesion is particularly important in high humidity and high temperature environments, where there is an increased risk of delaminating or "peeling" a polymer coating from a surface.

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Various adhesion promoters have been used in an effort to improve the adhesive strength and durability of adhesion of polymers to surfaces. Silane coupling agents have been used to improve, for example, the adhesion of polymer coatings to glass optical fibers, the consolidation of fillers and reinforcements into a polymeric resin matrix, and the water repellency of ceramics. Certain of these common silane coupling agents are described in United States Patent No. 5,527,835, issued June 18, 1996 to Shustack; other embodiments of this principle were elucidated by Warner et al. (WO 99/11454), Setiabudi (US 6,001,909), and Cagliostro et al. (*Journal of Advanced Materials* 1999, 31, 27-35). Commercially available organotitanate, aluminate, and -zirconate compounds such as those offered by Kenrich Petrochemicals, Inc. are also useful for improving the adhesion and compatibility of

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- polymers with a wide variety of mineral, metallic, inorganic, rubber, and plastic resin fillers, reinforcements, and surfaces (see, for example, (a) Monte, S. J. and Sugerman, G., Kenrich Petrochemicals, Inc., "Ken-React® Reference Manual - Titanate, Zirconate, and Aluminate Coupling Agents." (Bulletin KR 0395), 227 pages, (Summer 1993 – Second Revised Edition); (b) Monte, S. J. *Rubber Technology International* '96; (c) Dawson, B. *Rubber and Plastics News*, Sep. 21, 1998; (d) Monte, S. J. *Reinforced Plastics*, June 1996 and references therein) the disclosures of each of which are incorporated herein by reference.
- 10 It is known in the art to use organo-functional silanes to promote adhesion of polymer resins to glass surfaces. Organo-functional silane coupling agents used in the prior art include amino-functional silanes, acrylamido-functional silanes, allyl-functional silanes, vinyl-functional silanes, acrylate-functional silanes, methacrylate-functional silanes, and mercapto-functional silanes. Furthermore, academic and industrial
- 15 researchers have for many years been investigating a variety of methods for applying thin organic films to a myriad of surfaces (see, for example: (a) Ullman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: San Diego, 1991; (b) Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. *J. Am. Chem. Soc.* 1999, 121, 4088-9; (c) Duchet, J.; Chapel, J.-P., Chabert, B.; Gerard, J.-F. *Macromolecules* 1998, 31, 8264-72; (d) Zhao, B.; Brittain, W. J.; Vogler, E. A. *Macromolecules* 1999, 32, 796-800; (e) Bateman, J. E.; Eagling, R. D.; Worrall, D. R.; Horrocks, B. R.; Houlton, A. *Angew. Chem. Int. Ed.* 1998, 37, 2683-5; (f) Effenberger, F.; Götz, G.; Bidlingmaier, B.; Wezstein, M. *Angew. Chem. Int. Ed.* 1998, 37, 2462-4; (g) O'Brien, S.; Keates, J. M.; Barlow, S.; Drewitt, M. J.;
- 20 Payne, B. R.; O'Hare, D. *Chem. Mater.* 1998, 10, 4088-99; and references therein) the disclosures of which have appeared in the open literature and are incorporated herein by reference.
- Polyolefin compositions, including polydicyclopentadiene (poly-DCPD), may be
- 30 prepared using catalyzed olefin metathesis reactions such as, for example, ring opening metathesis polymerization (ROMP). Such olefin metathesis reactions and suitable metathesis catalysts (e.g., ruthenium- or osmium-based catalysts) have been previously described in, for example, United States Patent Nos. 5,312,940, 5,342,909, 5,728,917, 5,710,298, 5,831,108, and 6,001,909; PCT Publications WO 97/20865,
- 35 WO 97/29135 and WO 99/51344; in United States Provisional Patent Application No. 60/142,713 filed July 7, 1999 entitled "ROMP Reactions Using Imidazolidine-Based Metal Carbene Metathesis Catalysts;" and by Fürstner, Picquet, Bruneau, and Dixneuf in *Chemical Communications*, 1998, pages 1315-1316, the disclosures of each of which are incorporated herein by reference.

The aforementioned surface coupling agents, however, are not active in olefin ROMP reactions; rather, their efficacy as adhesion agents for ROMP polymers, such as poly-DCPD, is primarily the result of attractive London dispersion forces, also known as van der Waal's interactions, which are the weakest type of intermolecular forces.

- 5 Thus, there exists a need for metathesis-active adhesion agents that provide enhanced adhesion of ROMP polyolefins to various substrate surfaces by covalently incorporating such adhesion agents into these ROMP polyolefins.

SUMMARY OF THE INVENTION

- 10 The invention relates to novel adhesion agents that comprise compounds having at least one metathesis-active double-bond. More specifically, the invention provides metathesis-active adhesion agent compositions and methods for enhancing the adhesive strength and durability of adhesion of polymers produced by metathesis to substrate surfaces.

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The adhesion agents of the invention are useful for increasing the adhesion of various polyolefins to substrate surfaces including, but not limited to, silicate glasses and minerals, metals, metal alloys, ceramics, natural stones (e.g., marble and granite), plastics, carbon, silicon, and semiconductors. The adhesion agent compositions

20 comprise olefin compounds having at least one metathesis-active double-bond, which is defined as a double bond active in olefin cross-metathesis reactions or in ring-opening metathesis reactions such as, for example, ROMP reactions.

- In principle, any carbon-carbon double bond is capable of undergoing cross
- 25 metathesis reactions in the presence of a suitable olefin metathesis catalyst. Similarly, any cyclic olefin is capable of undergoing ring-opening by olefin metathesis. Accordingly, for example, when contacted with resins comprising dicyclopentadiene (DCPD) or other cyclic olefin in the presence of suitable ruthenium or osmium catalysts, the metathesis-active adhesion agents of the invention are covalently
- 30 incorporated into the bulk polymer backbone and thereby provide enhanced adhesion of the ring-opened polyolefin polymer to the substrate surface.

- The metathesis-active adhesion agents taught in the invention comprise compounds having at least one metathesis-active double bond and at least one compatibilizing
- 35 functionality capable of an attractive interaction with functional groups present at the (native or functionalized) substrate surface. Particularly preferred metathesis-active olefinic moieties include norbornenes, cyclopropenes, cyclobutenes, or other cyclic olefins. Particularly preferred compatibilizing functionalities include, for example,

- metal or silyl halides, ethers, and alkoxides for hydroxylated surfaces; acidic groups (e.g., carboxylic and mineral acids, boranes, alanes, and the like) for basic surfaces; basic groups (e.g., alkoxides, amines, phosphines, phosphine oxides, carboxylates, ethers, thioethers, and the like) for acidic surfaces; amphoteric groups such as
- 5 alcohols; and ionic groups, including ammonium, phosphonium, sulfonate, and conjugate ions of the weak acids and bases mentioned above, for ionic surfaces.

- One aspect of the invention is a novel metathesis-active adhesion agent. Another aspect of the invention is a method for enhancing adhesion of polyolefins to substrate
- 10 surfaces through the use of such adhesion agents. A further aspect of the invention is an article of manufacture, such as a molded part, comprising a polyolefin adhered to a substrate surface using a metathesis-active adhesion agent of the invention. These and other aspects of the invention will be apparent to one skilled in the art in light of the following detailed description of the preferred embodiments.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- The invention is directed to adhesion agents comprising olefin compounds having at least one metathesis-active double-bond. In certain preferred embodiments, the invention provides metathesis-active adhesion agent compositions, as well as methods
- 20 for enhancing the adhesive strength and durability of adhesion of polymers produced by metathesis to substrate surfaces.

- The metathesis-active adhesion agent compositions of the invention comprise compounds having at least one metathesis-active double-bond and at least one
- 25 compatibilizing functionality capable of interacting attractively with functional groups present at the substrate surface. These adhesion agents provide enhanced adhesion of a ring-opened polyolefin polymer to an underlying substrate surface through the covalent incorporation of the metathesis-active moiety into the bulk ROMP polymer while the compatibilizing functionality remains firmly bound to the substrate surface.
- 30 In preferred embodiments, the adhesion agents, when contacted with resins comprising dicyclopentadiene (DCPD) or other cyclic olefin in the presence of a suitable ruthenium or osmium catalyst, provide enhanced adhesion of the polyolefin polymer to the substrate surface.

- 35 In certain embodiments, the metathesis-active adhesion agents of the invention contain olefinic groups having metathesis-active double-bonds, thereby providing complementary functionality between the bulk polyolefin and the underlying substrate surface. Metathesis-active olefinic moieties include any terminal or internal, mono-,

di-, or trisubstituted olefins and any cycloalkene with at least three carbon atoms. Preferably, metathesis-active olefinic moieties include mono- or disubstituted olefins and cycloolefins containing between 3 and 200 carbons. Most preferably, metathesis-active olefinic moieties include cyclic or multicyclic olefins, such as cyclopropenes, 5 cyclobutenes, cycloheptenes, cyclooctenes, cyclooctadienes (COD), norbornenes, norbornadienes, [2.2.1]bicycloheptenes, [2.2.2]bicyclooctenes, benzocyclobutenes, cyclopentenes, cyclopentadiene oligomers including trimers, tetramers, pentamers, and the like; cyclohexenes, cyclohexenyl norbornenes, norbornene dicarboxylic anhydrides (nadic anhydrides), and substituted norbornenes including butyl 10 norbornene, hexyl norbornene, octyl norbornene, decyl norbornene, and the like. A preferred olefin monomer for use in the invention is dicyclopentadiene (DCPD). It is also understood that such compositions include frameworks in which one or more of the carbon atoms carry substituents derived from radical fragments including halogens, pseudohalogens, alkyl, aryl, acyl, carboxyl, alkoxy, alkyl- and arylthiolate, 15 amino, aminoalkyl, and the like, or in which one or more carbon atoms have been replaced by, for example, silicon, oxygen, sulfur, nitrogen, phosphorus, antimony, or boron. For example, the olefin may be substituted with one or more groups such as thiol, thioether, ketone, aldehyde, ester, ether, amine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, phosphate, phosphite, sulfate, sulfite, sulfonyl, 20 carbodiimide, carboalkoxy, carbamate, halogen, or pseudohalogen. Similarly, the olefin may be substituted with one or more groups such as C₁-C₂₀ alkyl, aryl, acyl, C₁-C₂₀ alkoxide, aryloxide, C₃-C₂₀ alkyldiketonate, aryldiketonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, arylthio, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, C₁-C₂₀ alkylphosphate, arylphosphate, wherein the moiety 25 may be substituted or unsubstituted.

An exemplary aspect of the invention is that metathesis-active adhesion agents for any surface composition can be designed based on the principles taught herein. Those skilled in the art understand that the surface chemistry of a particular composition 30 dictates the chemical and/or physical processes and reactions required to bond to said surface. For example, preferred adhesion agents for glass, silicon, or other hydroxylated surface compositions comprise compounds prepared by contacting silicon tetrachloride (SiCl₄) or silyl ethers with nucleophilic reagents including water, alcohols, amines, amides, phosphines, phosphides, carbanions, and alkoxides where 35 the proportion of nucleophile to silicon in such reactions is between about 1:1 and about 3:1 parts by mole. For example, a particularly preferred adhesion agent is prepared by the reaction of SiCl₄ under anhydrous conditions with 0.25 equivalent of 5-norbornene-2-methanol in the presence of a proton scavenger such as triethylamine. Preferred adhesion agents for a gold surface, on the other hand, are most appropriately

functionalized with thiol-containing compounds, whereas preferred agents for carbon black or titanium dioxide include titanates and zirconates. One preferred adhesion agent composition is using a norbornene where the compatibilizing functionality is of the formula $\text{SiCl}_x(\text{ER})_{3-x}$, wherein x is in the range of 0 to 3; E may be carbon, silicon, nitrogen, phosphorus, antimony, or oxygen; and R is an alkyl or aryl and may be substituted or unsubstituted. A particularly preferred composition is where the olefin is 5-norbornene-2-methoxy, x is 0 or 3, E is oxygen, and R is methyl or ethyl.

Particularly preferred compatibilizing functionalities will therefore be chosen based upon on the exact nature of the surface to be modified and include, for example, metal and silyl halides, ethers, and alkoxides for hydroxylated surfaces; substituted or unsubstituted olefins such as C_3 - C_{20} terminal olefins, or aldehydes for silicon surfaces, acidic groups (c.g., carboxylic and mineral acids, boranes, alanes, and the like) for basic surfaces; basic groups (e.g., alkoxides, amines, phosphines, phosphine oxides, carboxylates, ethers, thioethers, and the like) for acidic surfaces; amphoteric groups such as alcohols; and ionic groups, including ammonium, phosphonium, sulfonate, sulfonyls, and conjugate ions of the weak acids and bases mentioned above, for ionic surfaces; alkyl and aryl phosphine oxides; organotin, -aluminate, and -zirconate groups have proven effective for many of the above mentioned surfaces, including fiberglass and woven glass; inorganic fillers such as carbonates, alumina trihydrate, rutile; carbon black, rubber particles, and carbon and polymeric fibers and fabrics. A particularly preferred compatibilizing functionality is a silsesquioxane.

The metathesis-active adhesion agents taught in the invention may be formulated for use with any of a variety of substrate surfaces including, but not limited to, silicate glasses, metals, metal alloys, ceramics, natural stones (e.g., marble and granite), and plastics. Substrate surface refers not only to an uncoated substrate but also to a coated surface, such as, for example a glass substrate coated with metal. It is unnecessary that the substrate surface be smooth, flat, or non-porous for the practice of the invention. For example, fibrous surfaces, woven surfaces, microparticulate surfaces, glass surfaces, ceramic surfaces, metal surfaces, carbon surfaces, and polymer surfaces may be utilized in connection with the invention, in addition to substantially large, flat, regular, or monolithic articles. The invention may also be used in conjunction with variable density polyolefin compositions that provide, for example, a substrate or coated surface. Such variable density polyolefin compositions have been described in for example, U.S. Provisional Patent Application Serial No. 60/118,865 filed February 5, 1999 and U.S. Patent Application Serial No. _____, filed February 4, 2000, entitled "Polyolefin Compositions Having Variable Density and Methods for their

Production and Use," the contents of each of which are incorporated herein by reference.

5 The adhesion agents of the invention may be used to functionalize the native substrate surface prior to metathesis polymerization, or included as a component in the polymerizable resin composition, or both. In other words, the adhesion agent may be applied to or contacted with the substrate surface to functionalize (i.e., pre-treat) the surface prior to application of the resin to the surface. In this manner, the surface is provided with functional groups that are complementary to those contained in the applied polymer resin. The adhesion agent may be alternatively or additionally included in the resin formulation to be applied to the substrate, with the exception of adhesion agents containing terminal alkyl, amine, vinyl ether, thiol, and certain other functions known in the art to inhibit polymerization at higher than interfacial concentrations.

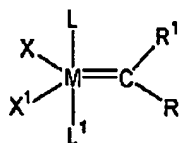
15 In the invention, the adhesive interaction between the native or pre-treated substrate surface and the bulk ring-opened polymer may be ionic/electrostatic, nonionic, and/or covalent in nature. The complementary functionalities provided by the adhesion agents of the invention provide "anchors" between the substrate surface and the bulk polyolefin that result in enhanced adhesive strength over silane, zirconate, titanate, aluminate and other conventional, non-metathesis-active coupling agents.

25 The polyolefin compositions or resins may be prepared using one or more monomers such as dicyclopentadiene, cyclopropene, cyclobutene, benzocyclobutene, cyclopentene, cyclopentadiene oligomers including trimers, tetramers, pentamers, and the like, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, unsubstituted norbornenes, substituted norbornenes such as butyl norbornene, hexyl norbornene, octyl norbornene, decyl norbornene, and the like; cyclohexenyl norbornene, norbornene dicarboxylic anhydride (nadic anhydride), norbornadiene, [2.2.1]bicycloheptene, and [2.2.2]bicyclooctene. These olefin monomers may be used alone or mixed with each other in various combinations to adjust the properties of the olefin monomer composition. For example, mixtures of cyclopentadiene dimer and trimers offer a reduced melting point and yield cured olefin copolymers with increased mechanical strength and stiffness relative to pure poly-DCPD. As another example, incorporation of COD, norbornene, or alkyl norbornene comonomers tend to yield cured olefin copolymers that are relatively soft and rubbery. A preferred olefin monomer for use in the invention is dicyclopentadiene (DCPD). In addition, the resin may be substituted or unsubstituted. In polyolefin resins that are substituted, the substitution may be any moiety such as thiol, thioether, ketone, aldehyde, ester, ether,

aminc, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carboimide, carboalkoxy, carbamate, halogen, and pseudohalogen. Similarly, the polyolefin resin may be substituted with a moiety such as C₁-C₂₀ alkyl, aryl, acyl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkylidicketonate, arylidicketonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, arylthio, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, wherein the moiety may be substituted or unsubstituted.

The polyolefin compositions for use with the invention may be prepared by any standard method for the ring-opening metathesis of olefin monomers (e.g., DCPD) using a metal carbene metathesis catalyst system. Ruthenium and osmium carbene compounds have been identified as particularly effective catalysts for ROMP reactions. Exemplary olefin metathesis reactions and suitable metathesis catalysts are described in, for example, United States Patent Nos. 5,312,940, 5,342,909, 5,728,917, 5,710,298, 5,831,108, and 6,001,909; PCT Publications WO 97/20865, WO 97/29135 and WO 99/51344; in United States Provisional Patent Application No. 60/142,713 filed July 7, 1999 entitled "ROMP Reactions Using Imidazolidine-Based Metal Carbene Metathesis Catalysts;" and by Filstner, Picquet, Bruneau, and Dixneuf in Chemical Communications, 1998, pages 1315-1316, the disclosures of each of which are incorporated herein by reference.

Any suitable metathesis catalyst may be used. Illustrative examples of suitable catalysts include ruthenium and osmium carbene catalysts as disclosed by U.S. Patent Nos.: 5,342,909; 5,312,940; 5,728,917; 5,750,815; 5,710,298, 5,831,108, and 5,728,785, all of which are incorporated herein by reference. Briefly, the ruthenium and osmium carbene catalysts possess metal centers that are formally in the +2 oxidation state, have an electron count of 16, are penta-coordinated, and are of the general formula



wherein:

M is ruthenium or osmium;

X and X' are each independently any anionic ligand;

L and L' are each independently any neutral electron donor ligand;

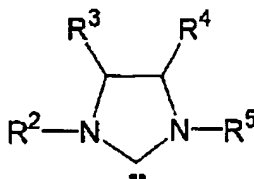
R and R' are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀

carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl.

Optionally, each of the R or R¹ substituent group may be substituted with one or more moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl which in turn may each be further substituted with one or more groups selected from a halogen, a C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl. Moreover, any of the catalyst ligands may further include one or more functional groups. Examples of suitable functional groups include but are not limited to: hydroxyl, thiol, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, and halogen.

In preferred embodiments of these catalysts, the R substituent is hydrogen and the R¹ substituent is selected from the group consisting C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, and aryl. In even more preferred embodiments, the R¹ substituent is phenyl or vinyl, optionally substituted with one or more moieties selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, and a functional group. In especially preferred embodiments, R¹ is phenyl or vinyl substituted with one or more moieties selected from the group consisting of chloride, bromide, iodide, fluoride, -NO₂, -NMe₂, methyl, methoxy and phenyl. In the most preferred embodiments, the R¹ substituent is phenyl.

In preferred embodiments of these catalysts, L and L¹ are each independently selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether. In more preferred embodiments, L and L¹ are each a phosphine of the formula PR³R⁴R⁵, where R³, R⁴, and R⁵ are each independently aryl or C₁-C₁₀ alkyl, particularly primary alkyl, secondary alkyl or cycloalkyl. In the most preferred embodiments, L and L¹ ligands are each selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, -P(isopropyl)₃, and -P(phenyl)₃. Another preferred embodiment of the catalyst is where L is any neutral electron donor and L¹ is an imidazolidine ligand. In certain embodiments, L¹ may have the general formula



wherein:

5 R^2 , R^3 , R^4 , and R^5 are each independently hydrogen or a substituent selected from the group consisting of C_1 - C_{20} alkyl, C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxycarbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl. R^3 and R^4 may also together form a cycloalkyl or an aryl moiety. A preferred embodiment is where R^3 and R^4 are both hydrogen or phenyl and R^2 and R^5 are each independently substituted or unsubstituted aryl. In addition, L and L' together may comprise a bidentate ligand.

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In preferred embodiments of these catalysts, X and X' are each independently hydrogen, halide, or one of the following groups: C_1 - C_{20} alkyl, aryl, C_1 - C_{20} alkoxide, aryloxy, C_3 - C_{20} alkyldiketonate, aryldiketonate, C_1 - C_{20} carboxylate, arylsulfonate, C_1 - C_{20} alkylsulfonate, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl, or C_1 - C_{20} alkylsulfinyl.

15 Optionally, X and X' may be substituted with one or more moieties selected from the group consisting of C_1 - C_{10} alkyl, C_1 - C_{10} alkoxy, and aryl which in turn may each be further substituted with one or more groups selected from halogen, C_1 - C_5 alkyl, C_1 - C_5 alkoxy, and phenyl. In more preferred embodiments, X and X' are halide, benzoate, C_1 - C_5 carboxylate, C_1 - C_5 alkyl, phenoxy, C_1 - C_5 alkoxy, C_1 - C_5 alkylthio, aryl, and C_1 -

20 C_5 alkyl sulfonate. In even more preferred embodiments, X and X' are each halide, CF_3CO_2 , CH_3CO_2 , CFH_2CO_2 , $(CH_3)_2CO$, $(CF_3)_2(CH_3)CO$, $(CF_3)(CH_3)_2CO$, PhO, MeO, EtO, tosylate, mesylate, or trifluoromethanesulfonate. In the most preferred embodiments, X and X' are each chloride. In addition, X and X' together may comprise a bidentate ligand.

25

Other additives and ingredients may be included in the resin formulations used in conjunction with the invention. Typical additives and reinforcements known in the art include, for example, antioxidants and stabilizers, flame retardants, dyes, pigments, fibers and fillers.

30

The invention is also directed to articles of manufacture, such as a molded part, comprising at least one polyolefin resin, at least one substrate surface, and at least one adhesion agent. Furthermore, the compositions and articles of manufacture of the invention are not limited to a single polymer-surface interface but include also

35 multilayers and laminates containing multiple polymer-surface interfaces, i.e., multilayer laminate articles can be assembled from different layers of similar or dissimilar materials. Such articles have found use in the production of, for example, ballistic panels, "bullet proof" glass, armor, and composite structural members. An example of such a

lamine structure would be layers of metal, glass, ceramic, and plastic incorporated into a single article using ROMP polyolefin compositions and metathesis-active adhesion agents as adhesives or glues between each layer.

- 5 A particular advantage of the invention is the ability to choose adhesion agents appropriate for each surface. In this way, an unlimited number of different layers, each of a different composition, can be consolidated into a single article using a single ROMP polyolefin composition as "glue" between each layer. Additionally or alternatively,
- 10 more than one ROMP polyolefin can be used in such multilayer articles, as in, for example, a metal-glass-plastic article wherein the ROMP polyolefin between the metal and glass layers is stiff and strong, while that between the glass and plastic layers is soft and rubbery.
- 15 Polyolefin coatings permitted by the invention can also serve the purpose of protecting or sealing the articles to which they are applied, such as in articles and applications including, for example, water- and weatherproofing, ablative and other sacrificial coatings, lithographic or other masks, and applications wherein the seal between two surfaces must be
- 20 impermeable to inert or reactive gases and liquids.

For the purposes of clarity, the specific details of the invention will be illustrated with reference to especially preferred embodiments. However, it should be appreciated that these embodiments and examples are for the purposes of illustration only and are

25 not intended to limit the scope of the invention.

EXAMPLES

Example 1

Preparation of Norbornene-Based Adhesion Agent

- 30 A 100 ml Schlenk tube equipped with a magnetic stirring bar was charged with SiCl_4 (Aldrich, 50 ml of 1.0 M solution in CH_2Cl_2), followed by addition of 8 ml of NEt_3 . To the stirred SiCl_4 solution was slowly added 6 ml of 5-norbornene-2-methanol (Aldrich), evolving heat and a copious amount of white precipitate. After the addition of the 5-norbornene-2-methanol was complete, the reaction was allowed
- 35 to stir at room temperature overnight. Cannula filtration of the pale yellow reaction mixture yielded a yellow CH_2Cl_2 solution of the norbornene-functionalized adhesion agent.

Example 2

Adhesion of Poly-DCPD to Octyltriethoxysilane (OTES)-Treated Glass Surface

A visually clean piece of plate glass was treated by pouring 5 mL neat OTES onto the substrate and allowing the liquid to stand for 15 h. The remaining liquid was
5 wiped away and the substrate was placed in a 40 °C oven. An activated DCPD resin at 40 °C – comprising dicyclopentadiene (BF Goodrich Ultrene 99), Ethanox 702 (Albemarle), triphenylphosphine (Strem), and metathesis catalyst dichloro(dimethylvinylmethylidene)bis(tricyclopentylphosphine)ruthenium in the proportions 1000:30:1:1 parts by weight, respectively – was poured onto the treated
10 glass and subjected to a cure cycle of 1 h at 40 °C, 2 h at ambient, 1 h at 140 °C. The hardened DCPD resin could easily be removed from the substrate by hand, indicating weak adhesion.

Example 3

Adhesion of Poly-DCPD to Metathesis-Active Allyltriethoxysilane (ATES)-Treated Glass Surface

The procedure of Example 2 was repeated except 5 mL neat ATES was used to treat the glass substrate. When attempting to remove the hardened DCPD resin from the glass surface, areas of cohesive failure were observed in the glass substrate.
20

Example 4

Adhesion of Poly-DCPD to Norbornene-Based, Metathesis-Active Silane-Treated Glass Surface

A 6" x 6" panel of plate glass was cleaned with Windex™ (Johnson Wax),
25 rinsed with acetone, and allowed to air dry. A 1 ml aliquot of the adhesion agent prepared in Example 1 was drawn into a syringe and dispensed directly onto the clean glass surface, resulting in copious evolution of gaseous HCl. The solution was allowed to dry on the glass surface, yielding a colorless, gelatinous film. The functionalized surface was then repeatedly washed with portions of toluene, acetone,
30 and water, followed by a final rinse with acetone. The functionalized glass plate was assembled into a mold with an untreated glass panel and the mold was then heated to 40°C.

The mold was then filled with poly-DCPD resin prepared by stirring in a flask: 92 g of DCPD monomer and 2.8g of Ethanox 702 antioxidant. This mixture was
35 stirred and heated to 35°C, and 0.09g of triphenylphosphine (PPh₃, or TPP) and 0.1 g of dimethylvinylmethylidenebis(tricyclopentylphosphine)ruthenium dichloride catalyst were added. The resulting resin was cured at 40°C for 30 minutes.

The mold was allowed to cool to ambient temperature for 2 hours and then was subjected to a 1 hour post-cure at 130°C. After post-cure, the untreated glass

panel was easily removed while the molded plaque was still cooling. As the poly-DCPD plaque cooled and shrank, the strain introduced by adhesion of the polymer to the functionalized surface resulted in catastrophic cohesive failure within the treated glass substrate. Examination revealed that several large scallops of glass had been
5 torn from the glass panel and remained firmly adhered to the surface of the polymer plaque.

Example 5

Adhesion of Poly-DCPD to Gold-Coated Glass Surface Treated with an Ionic, 10 Norbornene-Based, Metathesis-Active Coupling Agent

A glass slide coated on only one side with gold metal is immersed for one minute in a solution of 2-dimethylaminoethanethiol hydrochloride (Aldrich, 0.1 g in 100 ml of water), rinsed with clean water, then immersed in an ambient temperature solution of sodium 5-norbornene-2-carboxylate (0.1 g in a 1:1 (by volume)
15 ethanol/water mixture), which is prepared by the neutralization of 5-norbornene-2-carboxylic acid with one equivalent of aqueous hydroxide ion. The temperature of the solution is then raised to 50°C and the slide is allowed to soak at this temperature for 12 hours. After cooling to ambient temperature, the functionalized glass slide is removed from the carboxylate solution and allowed to air dry at 40°C. The
20 functionalized glass slide is then immersed for 30-60 seconds in a freshly prepared poly-DCPD resin, prepared as in Example 2 above. The slide is removed from the poly-DCPD resin and subjected to the cure cycle as in Example 2. The poly-DCPD resin covering the unfunctionalized, non-gold coated side of the slide is easily peeled from the surface by hand, but the resin adhering to the functionalized gold-coated side
25 requires physical scraping in order to remove the polymer from the surface.

Example 6

Poly-DCPD Safety Coating for an Untreated Glass Bottle

A poly-DCPD resin prepared as in Example 2 is maintained at 40 °C. A 250
30 mL clear glass Boston bottle is heated to 80 °C in an oven and then dipped repeatedly into the thickening poly-DCPD resin until a persistent coating of gelled resin is apparent on the bottle. The coated bottle is allowed to cure for 1 h at 40 °C, 2 h at ambient, and 1 h at 140 °C. After cooling from the post cure, the cured DCPD resin on the bottle is loose and has shrunk away from the glass surface.

Example 7

Poly-DCPD Protective Coating for a Glass Bottle Treated with Norbornene-Based Metathesis-Active Coupling Agent

A bottle as in Example 6 except that the exterior of the bottle is first treated as follows: A norbornene-based coupling agent is prepared from 5-norbornene-2-methanol and chlorotriethoxysilane according to the procedure in Example 1. The dry bottle is dipped into this solution, rinsed with toluene and acetone, then air dried. After post-cure and cooling, the poly-DCPD coating is firmly affixed to the bottle and must be cut or sliced to be removed.

Example 8

Addition of Cross-Metathesis Active Coupling Agent ATES to Bulk Poly-DCPD Resin

An activated poly-DCPD resin was prepared as in Example 2 with the addition of 5 parts ATES per hundred parts DCPD. This resin was then poured onto a visually clean piece of plate glass and placed in a 40 °C oven to cure. After 3 h, the poly-DCPD resin had still not cured, as determined by the tacky softness of the sample and the strong smell of unpolymcrized dicyclopentadiene.

Example 9

Poly-DCPD Composite Panel with Volan-Sized Fabric

A preform consisting of 20 layers of Volan-sized 7781 E-Glass fabric was dried at 120 °C for at least 2 h, cooled to 40 °C, then impregnated with a DCPD resin prepared as in Example 2. The interlaminar shear strength – often used as a test of fiber-matrix adhesion – of this composite article was found to be $2,198 \pm 84$ psi as measured by the short-beam shear test (ASTM-D-2344).

Example 10

Poly-DCPD Composite Panel with Metathesis-Active ATES-Treated Volan-Sized Fabric

A composite panel as in Example 9, except the oven-dried Volan-sized glass fabric was subjected to the following pre-treatment: A solution of 10 g ATES was prepared in 100 g toluene. Each ply of the preform was soaked in this solution for approximately 30 s, then stacked neatly in a second pan. The remaining solution was then poured over the stacked plies and the preform allowed to stand in this liquid for ca. 15 h. The preform was then dried in a 40 °C oven for 24 h before infusing with poly-DCPD. Interlaminar shear strength of the resulting composite as measured by the short-beam shear test (ASTM-D-2344) was found to be $2,538 \pm 45$ psi.

Example 11Poly-DCPD Composite Panel with Norbornene-Based, Metathesis-Active Silane-Treated Volan-Sized Fabric

- A preform was impregnated as in Example 9, but in this case, the oven dried
- 5 fabric was further pre-treated as follows: A solution of the norbornene-based coupling agent prepared as in Example 1 was loaded into a 12 l. round-bottom flask equipped with a Schott flange that had been dried 2 h at 120 °C, then fitted with a gas inlet supplied with dry argon gas and cooled while flowing the dry gas through the vessel. The solution was diluted with ~350 mL of Aldrich Anhydrous Grade toluene,
- 10 and the preform plies were soaked in this solution for approximately 5 minutes. The sizing solution was then poured off and the plies were rinsed (ca. 1 min. per aliquot) with 3x100 mL toluene followed by 3x100 mL acetone. Finally, the plies were dried in a 40 °C oven for 15 h before being stored in a sealed, polyethylene bag for several weeks before impregnation. The interlaminar shear strength of the resulting composite
- 15 as measured by the short-beam shear test (ASTM-D-2344) was found to be 3,090 ± 288 psi.

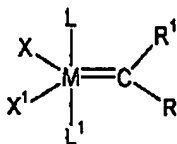
What is claimed is:

1. An adhesion agent composition comprising:
at least one $C_3 - C_{200}$ olefin compound having at least one metathesis active
5 double bond, wherein the olefin is substituted or unsubstituted; and
at least one compatibilizing functionality for interacting with a substrate
surface.
2. The composition of Claim 1 wherein the substrate surface is selected from the
10 group consisting of silicate glasses, silicate minerals, metals, metal alloys,
ceramics, natural stones, plastics, carbon, silicon, and semiconductors.
3. The composition of Claim 1 wherein the substrate surface is native or
functionalized.
- 15 4. The composition of Claim 1 wherein the olefin is selected from the group
consisting of norbornenes, cyclopropenes, cyclobutenes, benzocyclobutenes,
cyclopentenes, cyclopentadiene oligomers, cyclohexenes, cycloheptenes,
cyclooctenes, cyclooctadienes, norbornadienes, [2.2.1]bicycloheptenes, and
20 [2.2.2]bicyclooctene, cyclohexenylnorbornenes, and norbornene dicarboxylic
anhydrides.
5. The composition of Claim 4 wherein the olefin is dicyclopentadiene.
- 25 6. The composition of Claim 1 wherein the olefin is cyclic or multicyclic.
7. The composition of Claim 1 wherein the olefin is substituted with a moiety
selected from the group consisting of thiol, thioether, ketone, aldehyde, ester,
ether, amine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate,
30 phosphate, phosphite, sulfate, sulfite, sulfonyl, carbodiimide, carboalkoxy,
carbamate, halogen, and pseudohalogen.
8. The composition of Claim 1 wherein the olefin is substituted with a moiety
selected from the group consisting of $C_1 - C_{20}$ alkyl, aryl, acyl, $C_1 - C_{20}$ alkoxide,
35 aryloxy, $C_3 - C_{20}$ alkyldiketonate, aryldiketonate, $C_1 - C_{20}$ carboxylate,
arylsulfonate, $C_1 - C_{20}$ alkylsulfonate, $C_1 - C_{20}$ alkylthio, arylthio, $C_1 - C_{20}$
alkylsulfonyl, and $C_1 - C_{20}$ alkylsulfinyl, wherein the moiety is substituted or
unsubstituted.

9. The composition of Claim 1 wherein at least one carbon in the olefin is replaced by a group selected from the group consisting of silicon, oxygen, sulfur, nitrogen, phosphorus, antimony, and boron.
- 5 10. The composition of Claim 1 wherein the compatibilizing functionality is prepared from a group selected from the group consisting of metal halides, silyl halides, C₁-C₂₀ alkyls, ethers, esters, organic and mineral acids and their halides, aldehydes, boranes, alanes, alkoxides, amines, amides, phosphines, phosphides, carboxylates, thioethers, alcohols, sulfonates, sulfonyls, 10 ammonium, phosphonium, alkyl phosphine oxides, and aryl phosphine oxides.
11. The composition of Claim 1 wherein the compatibilizing functionality and the olefin are the same compound.
- 15 12. The composition of Claim 1 wherein the compatibilizing functionality is a silane prepared by contacting silicon halide or silyl ether with one or more nucleophilic reagents selected from the group consisting of water, alcohol, amine, amide, phosphine, phosphide, carbanion, and alkoxide.
- 20 13. The composition of Claim 1 wherein the olefin is a norbornene and the compatibilizing functionality is SiCl_x(ER)_{3-x}, wherein x is in a range of 0 to 3, E is selected from the group consisting of carbon, silicon, nitrogen, phosphorus, antimony, and oxygen; and R is C₁-C₂₀ alkyl or aryl, wherein R is substituted or unsubstituted.
- 25 14. The composition of Claim 13 wherein the olefin is 5-norbornene-2-methoxy, x is 0 or 3, E is oxygen, and R is methyl or ethyl.
15. The composition of Claim 1 wherein the compatibilizing functionality is a silsesquioxane. 30
16. The composition of Claim 1 wherein the substrate surface is selected from the group consisting of fibrous surfaces, woven surfaces, microparticulate surfaces, glass surfaces, ceramic surfaces, metal surfaces, carbon surfaces, 35 polymer surfaces, and semiconductor surfaces.
17. A method for adhering a polyolefin resin to a substrate surface comprising: pretreating the substrate surface by applying an adhesive agent to the substrate surface, the adhesive agent comprising at least one C₃-C₂₀₀ olefin compound

having at least one metathesis active double bond, wherein the olefin is substituted or unsubstituted; and at least one compatibilizing functionality for interacting with the substrate surface; and
 5 applying the polyolefin resin to the pretreated surface in the presence of a metal carbene metathesis catalyst.

18. The method of Claim 17 wherein the polyolefin resin is prepared via a ring opening metathesis polymerization of a cyclic olefin.
- 10 19. The method of Claim 17 wherein the polyolefin resin is prepared from one or more monomers selected from the group consisting of cyclopropenes, cyclobutenes, benzocyclobutenes, cyclopentenes, cyclopentadiene oligomers, cyclohexenes, cycloheptenes, cyclooctenes, cyclooctadienes, norbornenes, norbornadienes, [2.2.1]bicycloheptenes, [2.2.2]bicyclooctenes,
 15 cyclohexenylnorbornenes, and norbornene dicarboxylic anhydrides; and wherein the resin is substituted or unsubstituted.
20. The method of Claim 17 wherein the polyolefin resin is poly-DCPD.
- 20 21. The method of Claim 17 wherein the polyolefin resin is substituted with a moiety selected from the group consisting of thiol, thioether, ketone, aldehyde, ester, ether, amine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, halogen, and pseudohalogen.
- 25 22. The method of Claim 17 wherein the polyolefin resin is substituted with a moiety selected from the group consisting of C₁-C₂₀ alkyl, aryl, acyl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkylidenedione, arylidenedione, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, arylthio, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, wherein the moiety is substituted or
 30 unsubstituted.
23. The method of Claim 17 wherein the catalyst is of the formula:



wherein:

M is ruthenium or osmium;

X and X¹ are either the same or different and are any anionic ligand;

L and L¹ are either the same or different and are any neutral electron donor;

5 R and R¹ are either the same or different and are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl, wherein each of the
10 substituents is substituted or unsubstituted.

24. The method of Claim 23 wherein the substituent group is substituted with one or more substituted or unsubstituted moieties selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl.

25. The method of Claim 24 wherein the moiety is substituted with one or more groups selected from the group consisting of halogen, C₁-C₅ alkyl, C₁-C₅ alkoxy, and phenyl.

26. The method of Claim 23 wherein R is hydrogen and R¹ is selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, aryl, unsubstituted phenyl, substituted phenyl, unsubstituted vinyl, and substituted vinyl; and wherein the substituted phenyl and substituted vinyl are each independently substituted with one or more groups selected from the group consisting of C₁-C₅ alkyl, C₁-C₅ alkoxy, phenyl, hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen.

27. The method of Claim 23 wherein L and L¹ are each independently selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, imine, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether.

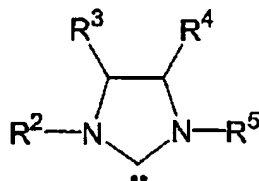
28. The method of Claim 23 wherein L and L¹ are each a phosphine of the formula PR³R⁴R⁵ wherein R³, R⁴, and R⁵ are each independently selected from the group consisting of aryl and C₁-C₁₀ alkyl.

29. The method of Claim 23 wherein L and L¹ comprise a bidentate ligand.

30. The method of Claim 23 wherein L is any neutral electron donor and L¹ is an imidazolidine ligand.

31. The method of Claim 30 wherein L¹ has the general formula:

5



wherein:

10 R², R³, R⁴, and R⁵ are each independently hydrogen or a substituent selected from the group consisting of C₁-C₂₀ alkyl, C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl.

15 32. The method of Claim 31 wherein R³ and R⁴ together form a cycloalkyl or an aryl moiety.

33. The method of Claim 31 wherein R³ and R⁴ are both hydrogen or phenyl and R² and R⁵ are each independently substituted or unsubstituted aryl.

20

34. The method of Claim 23 wherein X and X¹ are each independently selected from the group consisting of hydrogen, halogen, substituted moiety and unsubstituted moiety, wherein the moiety is selected from the group consisting of C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkylidicktonate, 25 arylidicktonate, C₁-C₂₀ carboxylate, arylsulfonate, C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl, and wherein the moiety substitution is selected from the group consisting of C₁-C₁₀ alkyl, C₁-C₁₀ alkoxy, and aryl.

30 35. The method of Claim 23 wherein X and X¹ are each independently selected from the group consisting of halide, benzoate, C₁-C₃ carboxylate, C₁-C₃ alkyl, phenoxy, C₁-C₃ alkoxy, C₁-C₃ alkylthio, aryl, and C₁-C₃ alkyl sulfonate.

36. The method of Claim 23 wherein X and X' are each independently selected from the group consisting of halide, CF_3CO_2 , CH_3CO_2 , CFH_2CO_2 , $(\text{CH}_3)_2\text{CO}$, $(\text{CF}_3)_2(\text{CH}_3)\text{CO}$, $(\text{CF}_3)(\text{CH}_3)_2\text{CO}$, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate.
37. The method of Claim 35 wherein X and X' are both chloride.
38. The method of Claim 23 wherein X and X1 comprise a bidentate ligand.
39. A method for adhering a polyolefin resin to a substrate surface comprising: contacting a polyolefin resin with an adhesion agent in the presence of a metal carbene metathesis catalyst to form a resin/agent mixture, the adhesion agent comprising at least one $\text{C}_3 - \text{C}_{200}$ olefin compound having at least one metathesis active double bond, wherein the olefin is substituted or unsubstituted; and at least one compatibilizing functionality for interacting with the substrate surface; and applying the mixture to the substrate surface.
40. The method of Claim 39 wherein the polyolefin resin is poly-DCPD.
41. An article of manufacture comprising:
at least one polyolefin resin;
at least one substrate surface; and
at least one adhesion agent, the adhesion agent comprising at least one $\text{C}_3 - \text{C}_{200}$ olefin compound having at least one metathesis active double bond, wherein the olefin is substituted or unsubstituted; and at least one compatibilizing functionality for interacting with the substrate surface; wherein the polyolefin resin is adhered to the adhesion agent; and wherein the adhesion agent is adhered to the substrate surface.
42. The article of Claim 41 further comprising a plurality of polyolefin resin-to-substrate adhesions.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03002

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 4/80, 4/06, 263/04; C08K 3/14, 3/22

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/81, 435, 437, 440, 442; 526/171, 177, 281, 283, 284; 556/13, 21, 58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Journal of American Chemical Society, Organometallics, Journal of Organometallic Chemistry

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

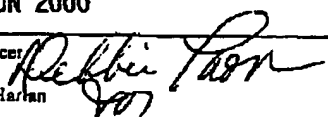
EAST (search terms: carbene, ruthenium, osmium and adhesive)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 6,020,443 A (WOODSON et al) 01 February 2000, col. 3, line 66 through col. 9, lines 28.	1-42
X, P	US 5,939,504 A (WOODSON et al) 17 August 1999, col 6, line 19 through col. 10, line 19.	1-42
X	US 5,849,851 A (GRUBBS et al) 15 December 1998, col. 2, line 37 through col. 6, line 39.	1-42
X, P	US 5,969,170 A (GRUBBS et al) 19 October 1999, col. 2, line 42 through col. 8, line 59.	1-42
X, P	US 5,932,664 A (CHEN et al) 03 August 1999, col. 2, line 27 through col. 5, line 8.	1-42

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	'I' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
'A' document defining the general state of the art which is not considered to be of particular relevance	'X' document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
'E' earlier document published on or after the international filing date	'Y' document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combinations being obvious to a person skilled in the art
'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	'A' document member of the same patent family
'O' document referring to an oral disclosure, use, exhibition or other means	
'P' document published prior to the international filing date but later than its priority date claimed	

Date of the actual completion of the international search 18 MAY 2000	Date of mailing of the international search report 13 JUN 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 306-3429	Authorized officer:  Robert D. Harlan Telephone No. (703) 306-5926

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03002

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,880,231 A (GRUBBS et al) 09 March 1999, col. 2, line 37 through col. 5, line 8.	1-42
X	US 5,728,785 A (GRUBBS et al) 17 March 1998, col. 4, line 19 through col. 6, line 57.	1-42
Y, P	HUANG et al. Olefin Metathesis-Active Ruthenium Complexes Bearing a Nucleophilic Carbene Ligand, JACS March 1999, 121, 2674-2678.	1-42

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/03002

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

524/81, 435, 437, 440, 442; 526/171, 172, 281, 283, 284; 556/13, 21, 58